METHOD FOR FORMING COLORED CELLULOSIC MATERIALS

Inventor: Matthew A. Szymanski

Attorneys for Applicants:
Boyle, Fredrickson, Newholm,
Stein & Gratz, S.C.
250 Plaza, Suite 1030
250 East Wisconsin Avenue
Milwaukee, WI 53202
Telephone: (414) 225-9755
Facsimile: (414) 225-9753
Attorney Docket No.: 381.047

METHOD FOR FORMING COLORED CELLULOSIC MATERIALS

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority from U.S. Provisional Patent Application Serial No. 60/437,978, which was filed on January 3, 2003.

FIELD OF THE INVENTION

The present invention relates to dyeing processes, and more specifically to methods for dyeing paper and other cellulosic materials.

BACKGROUND OF THE INVENTION

On many occasions, it is desired to utilize a cellulosic material product, such as paper, linerboard, paperboard and/or cardboard, that has a specific color for a particular use. For example, when decorating for a special occasion, streamers of various colors are often utilized to provide a festive appearance to the location at which the occasion is being celebrated.

In order to form products formed of a cellulosic material and having a desired color, many different dying techniques have been utilized. While many of these dyeing techniques provided adequate color to the cellulosic material being dyed when finished, a significant problem remained in that the dye often times washed out or bled from the cellulosic material either during the dying process or when the material was contacted by a liquid or simply rubbed against another surface.

In order to attempt to overcome the bleeding problem, a number of different dyeing compositions and methods were developed. For example, Reinhardt U.S. Patent No. 4,502,807 discloses a dye stuff that incorporates a thickening mixture including both a synthetic thickening agent and a polysaccharide. The presence of the thickening mixture with these components enhanced the ability of the dye to remain in the proper location on the textile to which the dye was applied. Further, Panto et al. U.S. Patent No. 4,398,915 discloses a method of preparing bleed resistant colored cellulosics utilizing a colored particle such as a dye/starch complex formed as a reaction product of a starch with a reactive dye compound and a chemical cross-linking agent. Further, Kiesewetter et al. U.S. Patent No. 5,384,585 discloses the printing of textiles using a dye composition including a reactive dye and a methylcarboxymethyl cellulose as a thickener.

However, these techniques, while initially providing the paper, linerboard, paperboard or cardboard product with the desired color and an increased level of resistance to bleed or color migration, do not achieve the desired level of resistance to the removal of the colored dye from the product. As a result, colored products are still produced in which the color bleeds from the product, or in which the color can be removed from the product by wetting and/or rubbing a colored surface of the product.

Therefore, it is desirable to develop a method for dying or otherwise coloring a cellulosic product in which the dye or color added to the product is highly resistant to removal from the product.

SUMMARY OF THE INVENTION

The present invention is an improved method for coloring cellulosic material products in which the color is applied to the product such that the color does not bleed and/or cannot be easily removed from the product. The method or process involves two separate steps which achieve the desired result of applying the color or dye to the product such that the dye is highly resistant to removal.

The first step in the method involves applying the colorant to the cellulosic substrate in any of a number of well-known application methods. The colorant applied to the cellulosic substrate is formed as an aqueous solution of a thickener, a dye, and water. The thickener can be virtually any suitable material used to thicken and stabilize a dye composition, as will be described. Also, a wide range of dyes can also be used in forming the colorant, as will be described. The colorant formed by the dye, thickener and water can be any suitable colorant used in the printing or dyeing of cellulosic materials and/or textiles that is able to be applied to the substrate in any of a number of conventional dye application methods and that resists any spreading or migration on the surface of the substrate after application.

In the second step, an overcoat material is applied to the substrate over the colorant in order to form a protective film over the colorant on the cellulosic material and increase the resistance to removal of the colorant from the substrate. The overcoat material essentially provides a barrier between the colorant and any liquid and/or surface that prevents contact with the colorant, thereby maintaining the colorant on the substrate.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is an improved method for applying a colorant to a cellulosic substrate in a two-step process which greatly improves the resistance to removal of the colorant on the substrate. While the method is applicable to the application of a colorant or dye to virtually any number of different substrate types, some of the preferred substrates which are capable of being utilized in this method include cellulosic substrates such as white-top linerboard, linerboard, and paper, among others.

In a particularly preferred embodiment of the method of the invention, the substrate is a white-top linerboard that is defined as a two-ply cellulosic web that has a basis weight of 20 pounds to 90 pounds per 1000 square feet. The base ply is comprised of a virgin material, recycled material or any combination thereof. The top ply of the cellulosic web is comprised of bleached or de-inked cellulosic fiber with a GE brightness of at least 60.

Another preferred substrate is linerboard which is defined as a two-ply cellulosic web that has a basis weight of 20 pounds to 90 pounds per 1000 square feet. The base ply is comprised of virgin material, recycled material, or any combination thereof. The top ply of the cellulosic web is comprised of recycled or virgin cellulosic fiber.

Still another preferred substrate is paper which is defined as a cellulosic web that has a basis weight of 20 pounds to 160 pounds per 3000 square feet. The web may also include filler materials including, but not limited to, clay, calcium carbonate, titanium dioxide, and/or sizing agents.

When applying the colorant to the desired substrate, in the first step, the colorant is added to the substrate in a suitable printing or dyeing process, such as either a conventional off-paper machine application, or an on-paper machine application, including via a size press or water box. Some suitable off-paper machine application processes can include, but are not limited to, flexographic application, rod application, and/or processes utilizing air-knife coaters.

The colorant is most preferably comprised of a solution of a thickener, the pigment, and/or dye stuff, and water in the following proportions:

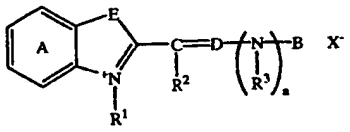
1–30% by weight dye stuff and/or pigment;

1–15% by weight a first thickener;

1–5% of an optional second thickener (in lieu of or in addition to the first thickener) for rheology modification; and

the balance, water.

With particular regard to the dye stuff or pigment, the dye stuff for the purposes of this disclosure is defined as any compound within the class of either basic dyes or anionic direct or fiber reactive dyes, or a pigment that can impart a color to a cellulosic material such as a dry coloring matter, usually an insoluble powder to be mixed with water, oil or another base to produce paint in similar products. More particularly, in one aspect of the present invention, there is thus provided a colorant comprising, as a direct dye, a compound represented by the following formula (1):



wherein, ring A represents a benzene ring which may have a substituent or may further be cyclocondensed with another aromatic ring;

B represents an aryl group which may have a substituent or may be coupled with R^2 to form a heterocyclic structure which will be described later, or a heterocyclic group which may have a substituent or may be coupled with R^2 to form a heterocyclic structure which will be described later,

D represents a nitrogen atom or a group CR^4 (in which R^4 represents a hydrogen atom or a C_{1-6} alkyl group);

E represents a group NR^5, CR^6R^7 or $CR^6{=}CR^7$ (in which R^5 represents a C_{1-6} alkyl group which may have a substituent, a C_{2-6} alkenyl group which may have a substituent or an aryl group which may have a substituent, or forms, when taken together with R^2, a ring which will be described later, and R^6 and R^7 each independently represents a hydrogen atom or a C_{1-6} alkyl group), an oxygen atom or a sulfur atom;

R^1 represents a C_{1-6} alkyl group which may have a substituent, a C_{2-6} alkenyl group which may have a substituent or an aryl group which may have a substituent;

R^2 represents a divalent group bonded to B or forms, when taken together with R^3 or R^5, a ring which will be described later,

R^3 forms, when taken together with R^2, a ring which will be described later;

n stands for 0 or 1, with the proviso that when n=0, R^2 and R^5, when taken together with N—C—C, form a 5- to 7-membered nitrogen-containing heterocyclic structure which may have a substituent, or R^2 is bonded to B, thereby forming a 6- or 7-membered heterocyclic structure which may have a substituent and may contain a hetero atom other than D and when n=1, R^2 and R^3, when taken together with C=D—N, form a 5- to 7-membered nitrogen-containing heterocyclic structure which may have a substituent, and

X^- represents an anion.

In the formula (1), examples of the substituent which the ring A may have include alkyl groups, aryl groups, alkoxy groups, amino groups, hydroxy groups, cyano groups, nitro groups and halogen atoms, more specifically, methyl group, ethyl group, methoxy group, ethoxy group, chlorine atom and bromine atoms. Examples of the aromatic ring with which the ring A may be cyclocondensed include a benzene ring.

Examples of the aryl group represented by B include phenyl, 1-naphthyl and 2-naphthyl groups, while those of the heterocyclic group include 2-benzthiazolyl and 3-indolyl groups, each of which may be substituted with a chlorine atom, bromine atom, nitro group, cyano group, C_{1-4} alkyl group, phenyl group, benzyl group, C_{1-4} alkoxy group, hydroxy group, phenoxy group, benzyloxy group, C_{1-4} alkylsulfonyl group, phenylsulfonyl group, benzylsulfonyl group, aminocarbonyl group, mono- or di-(C_{1-4} alkyl)aminocarbonyl group, aminosulfonyl group, C_{1-4} alkylcarbonyl group, C_{1-4} alkylcarbonylamino group, benzoylamino group, phenylazo group, and a group NR^8R^9 (in which R^8 and R^9 each independently represents a hydrogen atom, C_{1-4} alkyl group, aryl group, aralkyl group, unsubstituted or mono- or di-(C_{1-4} alkyl)-substituted amino(C_{1-4} alkyl) group, amino(C_{1-4} alkyl) group substituted by a group of the formula (1) from which one hydrogen atom has been removed, or (C_{1-4} alkoxy) (C_{1-4} alkyl)amino group). The number of these substituents is 1 to 3. The cycle-constituting atom may be coupled with the above-exemplified substituent to form another cyclic structure.

Examples of the C_{1-6} alkyl group represented by R^4 in the case where D represents a group CR^4 or by R^6 or R^7 in the case where E represents a group $CR^6\ R^7$ or $CR^6{=}CR^7$ include methyl, ethyl, propyl, isopropyl and cyclohexyl groups. Preferred examples of R^4, R^6 or R^7 include hydrogen atom and methyl groups.

Examples of the C_{1-6} alkyl group represented by R^5 in the case where E represents a group NR^5 include methyl, ethyl, propyl, isopropyl and cyclohexyl groups; those of the C_{2-6} alkenyl group include ethenyl and propenyl groups; and those of the aryl include phenyl and naphthyl groups, each of which may be substituted with an aryl, alkoxy, amino, hydroxy or cyano group, or a halogen atom.

Examples of the C_{1-6} alkyl group represented by R^1 include methyl, ethyl, propyl, isopropyl and cyclohexyl groups, those of the C_{2-6} alkenyl group include ethenyl and propenyl groups, and those of the aryl group include phenyl and naphthyl groups, of which the alkyl group is preferred as R^1. Examples of the group which may be a substituent for them include aryl groups, cyano group, halogen atoms, hydroxy group, C_{1-4} alkoxy groups, $NR^{10}\ R^{11}$ (in which R^{10} and R^{11} each independently represents a hydrogen atom, C_{1-4} alkyl group, aryl group, aralkyl group, unsubstituted or mono- or di(C_{1-4} alkyl)substituted amino(C_{1-4} alkyl) group, or (C_{1-4} alkoxy) (C_{1-4} alkyl)amino group) and a group of the formula (1) from which one hydrogen atom has been removed.

Examples of the R^5 -R^2 or R^2 -R^3 in the case where a 5- to 7-membered nitrogen-containing heterocyclic structure which may have a substituent is formed by R^2 and R^5 when they are taken together with N—C—C at n=0, or by R^2 and R^3 when taken together with C=D—N at n=1, include groups represented by $-(CR^{12}\ R^{13})_m-$ (in which R^{12} and R^{13} each independently represents a C_{1-4} alkyl group and m stands for an integer of 2 to 4).

Examples of the divalent group, as R^2, bonded to B in the case where a 6- or 7-membered heterocyclic structure which may have a substituent and may have a hetero atom other than D is formed by bonding of R^2 to B when n=0 include groups —CH=N— and —CO—O—.

Examples of the anion represented by X^- include chloride ions, bromide ions, iodide ions, trichlorozincic acid ions, tetrachlorozincic acid ions, sulfuric acid ions, hydrosulfuric acid ions, methyl sulfate ions, phosphoric acid ions, formic acid ions and acetic acid ions.

The thickener utilized in the formation of the colorant may be selected from both synthetic and natural thickeners. More specifically, the composition of the thickeners used in the formation of the colorant can vary between a proportion of 0% for the synthetic thickener and 100% by weight for the natural thickener, and vice versa, depending upon the response of the products used to the disburse dye stuffs used. Mixtures which are more preferable regarding the dispersion stability of the dye stuffs contain between 1 to 30% by weight of the natural thickeners, and most preferably between 1 to 15%, and 1 to 10% by weight of the synthetic thickeners, and most preferably between 1 to 5%.

The synthetic thickenings are preferably carboxyl containing synthetic thickenings and the natural thickenings are based on polysaccharides in preferred embodiments of the invention. Examples of suitable carboxyl-containing synthetic thickenings which can be used according to the invention are aqueous solutions or gel-forming dispersions of polymerized low molecular weight monoethylenically or polyethylenically unsaturated monocarboxylic or dicarboxylic acids, such as polyacrylic acid and its homologs, for example products of polymerizing methacrylic acid or crytonic acid, and polymers of carboxyalkylderivatives, such as idaconic or teraconic acid, similarly aqueous solutions of or dispersions of polymerized maleic acid or its anhydride and fumaric acid and of its homologs, such as, for example, citriconic acid or mesaconic acid, further of copolymers of olefins, for example, ethylene, propylene or butadiene or of lowelalkylacrylates, optionally substituted acrylamids, vinyl alcohols, vinyl ethers, vinyl esthers, vinyl chloride, vinyl edene chloride, styrene, acrylonitrile, and analogous alkyl compounds and the above-mentioned monomers. These examples also include the reaction products of the polymers and copolymers described, with polyhydric alcohols and amines, or amino alcohols, and combinations of highly polymerized products with less highly polymerized products.

The polysaccharides used preferably as the natural thickeners according to the invention embrace optionally degraded and/or etherified natural products such as high molecular weight carob bean flour or guar flour and starch or cellulose ethers. In a particularly preferred embodiment, the thickener is formed only of material thickeners including carboxymethyl cellulose and starch.

While the components of the colorant can be mixed to form the colorant in any suitable manner, a particularly preferred method is _____.

After the colorant has been formed and applied to the selected surface of the cellulosic substrate, the substrate may be slightly dried to allow for a limited set of the colorant on the substrate and to prevent the smearing of the colorant from the substrate. Further, the colorant application rate can vary depending upon the color shade depth desired on the surface of the substrate. For example, in a preferred embodiment the application rate of the colorant is 1–40% by weight of the substrate and more preferably 1–15% by weight of the substrate.

After the application of the colorant to the substrate, in the second step of the method, a film of a suitable overcoat material is applied as an overcoat to the colored cellulosic substrate to impart the requisite wet and dry rub fastness for the colorant reacted onto the substrate. The application methods for the overcoat material are similar to printing or dyeing methods used for the application of the colorant and can include, but are not limited to, off-paper machine application methods, such as flexographic, rod, and/or knife air coaters. Further, with regard to the overcoat material the material is a natural or synthetic rubber formed from various compounds, including but not limited to polybutadiene, polyisobutylenes, polystyrenes, polyacrylates and polyurethanes. In a preferred embodiment the material is a latex, which for the purposes of this invention is defined as any material within the class of modified styrene butadiene-based polymers or modified styrene acrylate polymers with provisions for changes in polymer T_G value or polymer combination. More preferably, the overcoat may be a 50% solids latex product which is used as a "varnish" layer over the substrate, to provide wet and dry rub fastness and to add a gloss or matte finish to the substrate. Further, the overcoat application rate to the substrate can vary depending upon the level of fastness and the gloss level required for the substrate, with greater fastness properties and higher gloss achieved with a higher overcoat application rate. More specifically, in a preferred embodiment the application rate for the overcoat will be within a range of 1% to 25% by weight of the substrate and more preferably between 1% and 5% by weight of the substrate.

Colored linerboard produced as described may be used in any corrugated application, e.g. point of purchase displays or corrugated containers. Application of the overcoat material enhances printability of the material and ensures that the print medial does not bleed into the underlying dyed substrate

Various alternatives are contemplated as being within the scope of the following claims particularly pointing out and distinctly claiming the subject matter regarded as the invention.